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Large Dopant Dependence of the Current Limiting Properties of Intrinsic Conducting Polymer Surge Protection Devices

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Abstract

New two terminal surge protection devices based on intrinsic conducting polymers are demonstrated to be strongly affected by the dopant molecule type. Thermogravimetric analysis combined with current-voltage studies show a causal link between the dopant molecule, moisture content and the current limiting capability of the devices. Polyaniline thin-films with high moisture content produces devices with current saturation and foldback effects at high applied voltages while low moisture content films exhibit no current rectification and instead demonstrate decreasing resistivity with increasing voltage. Polyaniline doped with sulfuric acid (H_2SO_4) exhibited the largest moisture content and surge protection devices built with this material produced for the first time negative differential resistance in ambient conditions. A further improvement was made upon this through surface engineering of the interface between the polymer and electrodes using self-assembled monolayers.

Keywords: conducting polymer; polyaniline; surge protection; current limiter; moisture sensor; dopant dependence.

1. Introduction

Protection of electronic devices from power surges and spikes is essential in a world increasingly reliant on technology. Mobile phones, cameras and mp3 players require frequent re-charging and for people on the go this is often done using unfamiliar and unregulated power sources that can cause device failure. Electrostatic discharge (ESD), arising during the connection of cables or the user brushing against exposed pins in the connector, as well as Electrical Fast Transients (EFT), created when switching high current loads or introduced by inductive coupling, are also significant problems.[1] Thus there is significant advantage in having power regulation and circuit protection incorporated directly within devices on bus lines, recharging ports and audio jacks. As electronics continues to shrink available space is increasingly more of an issue and there is a need for lower cost and smaller footprint alternatives. Circuit protection is also important in many medium power applications.[2] The use of "dc microgrids" for homes and small businesses is an emerging trend due to rising energy costs and increased awareness of green energy. These systems involving solar panels, wind turbines, sensors, battery storage and backup-generators require the coordinated operation of electronic power converters with in-built fault tolerance to rapidly isolate short circuits for protecting equipment and maintaining continuity of power to loads.[3,4,5]

Circuit protection needs to be automatic, fast and invisible to the user, with re-setting occurring without user intervention. In the case of small portable electronic devices the circuit protection as well needs to be especially low cost, have a very small footprint (preferably PCB surface mounted) and consume virtually no energy so as to not incur additional load on the limited battery life. Various methods are used to protect devices from overvoltage and overcurrent conditions, examples include silicon avalanche diodes, Schottky diode surge protectors,[6] metal oxide varistors,[7,8] polymeric positive temperature coefficient devices[9], spark gaps[10] and gas arrestors.[11] Each having their own advantages and disadvantages and suitability to different applications.[12,13] Recently we reported a new type of surge protection device based on intrinsic conducting polymers (ICP).[14] Unlike many alternative circuit protection devices the ICP device has the advantage that it is consists of only a single inline element,

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which undergoes a transition from a low resistance state to a high resistance state when the current exceeds a critical value. The mechanism involves a partial de-doping of the polymer material due to removal of water during Joule heating. This causes the polymer material to increase in resistivity, thereby limiting further current flow in the device. After a current surge, cooling of the device occurs and water is quickly re-adsorbed into the nanoporous polymer structure, which re-dopes the polymer and switches the device back to its initial conducting state. This is very different to other Joule heating based circuit protection devices, such as polymeric positive temperature coefficient (PPTC), which instead are based upon metal or semiconductor materials embedded within an insulating polymer of high thermal expansion coefficient.[15,16] These devices operate by having many conduction pathways that break during a current surge due to joule heating and thermal expansion of the insulating polymer.[17,18,19,20] Upon cooling the polymer component shrinks to its previous state, re-establishing the conducting pathways and the device resumes normal operation.

Earlier we reported ICP devices that exhibited current saturation behaviour at high applied voltages[14] and recently we have shown their performance could be significantly improved via interface engineering using self-assembled monolayers (SAM).[21] SAM modified devices exhibited current foldback behaviour, which has the advantage that the current is not only limited but is reduced, thereby minimizing potential damage to circuit components or external devices. Neither of these previous papers examined the role of the dopant in the switching mechanism and its effect on the performance properties of the ICP devices. In this work we report a strong link between the current limiting properties of the films and the dopant molecule. Although it has been previously established that the presence of moisture enhances the conductivity of doped polyaniline[22, 23,24,25,26,27,28,29,30,31] we instead focus here on showing that the dopant molecule type controls the moisture content in the polymer film which in turn strongly affects the current limiting capability of the polymer films during overcurrent conditions. Based on these results, judicious selection of the polymer dopant is shown to be crucial for achieving desired device characteristics as well as important for improving the current limiting properties of the devices. For example here we show for the first time that foldback behaviour can be achieved in normal ambient humidity conditions when using sulfuric acid (H_2SO_4) as a dopant. Further, we show that by

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modifying the gold electrodes with self-assembled monolayers to make them hydrophobic this effect can be further enhanced.

2. Material and Methods

The conducting polymer current limiter device used in this work was similar to that previously reported.[14] The devices consist of a thermally insulating ceramic substrate with two top-deposited gold electrodes (4-6 μm thick) that are separated by a 55 μm gap containing the conducting polymer. An additional insulating layer (Dupont 5415A, 8-12 μm thick) covers the gold electrodes so as to define a circular electrode region (6.67 mm diameter) of fixed area for the electrochemical deposition of the polymer. We note here that the width and spacing of the gap as well as the polymer thickness can be used to tailor the size and current limiting properties of devices for different applications. The conducting polymer polyaniline is electrochemically deposited onto the gold electrodes using a bath consisting of 0.5 M aniline (Aldrich, 99.5%) and various dopant molecules. Table 1 lists the polymer dopants used in the study and concentration of the solutions used in the polymerization procedure. All polymerizations were carried out electrochemically except in the case of DBSA doped films, which was prepared by chemical means.[32] Thermogravimetric analyses (TGA) measurements were carried out by depositing polymer films on large area gold electrodes and scraping off the polymer until there was sufficient material for TGA measurements. A Perkin Elmer Instruments TGA was used for the procedure. The heating rate used was 10°C/min and the measurements were done from 20°C to 600°C. Fast I-V sweeps on the devices were used to simulate the conditions of a current surge and this was carried out using a home-built system consisting of a computer controlled power supply (0-12 V, 0-10 A) with 16 bit analogue to digital converters (200 kHz) for sourcing and reading of the voltage/current.[14] Modification of the gold electrodes by self-assembled monolayers was similar to that reported previously[21] and involved leaving the devices for 24 hours in an ethanol solution with 0.01 M of 1-dodecanethiol (DDT) $C_{12}H_{26}S$ (Aldrich, >98%). The SAMs were characterised using drop shape analysis using a Kruss DSA10 equipped with a CCD camera. The advancing and receding angle

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technique demonstrated a contact angle greater than 150° indicating the formation of a superhydrophobic surface.

Dopant Type and Concentration	**Aniline**	**Polymerization Method**
hydrochloric acid (HCl), 2.0 M in H_2O	0.5 M	Electrochemical
para toluenesulfonic acid (pTSA), 1.0 M in H_2O	0.25 M	Electrochemical
dodecylbenzensulfonic acid (DBSA), 0.22 in H_2O	0.22 M	Chemical
perchloric acid ($HClO_4$), 2.0 M in H_2O	0.5 M	Electrochemical
methane sulfonic acid (MSA), 2.0 M in H_2O	0.5 M	Electrochemical
sulfuric acid ($H2SO_4$), 2.0 M in H_2O	0.5 M	Electrochemical

Table 1. Table showing the monomer and dopant concentrations and polymerization method used for the preparation of each polymer type.

3. Results

Conducting polyaniline films prepared with six different dopant types was used to investigate the role of the dopant in electronic switching under current surge conditions. The dopant molecules were the following: hydrochloric acid (HCl), para toluenesulfonic acid (pTSA), dodecylbenzensulfonic acid (DBSA), perchloric acid ($HClO_4$), methane sulfonic acid (MSA) and sulfuric acid ($H2SO_4$). Thermogravimetric analyses was used to determine their moisture content and desorption profiles. Figure 1 shows the TGA results for the polyaniline films over the range of 20-200°C. Upon heating all of the polymers exhibited a decrease in their weight over the range of 30-130°C, which is the temperature at which water is typically known to desorb from the polymer.[33] For all of the polymers the onset of water desorption began at 30-40°C and was completed by 130°C. For MSA doped films, the dopant used in our previous studies, the TGA show that water desorption is maximum at 65°C and completed by 100°C. In contrast to MSA doped films water is bound more strongly in the H_2SO_4 doped films as shown by the desorption maximum at 80°C and a tail that extend until 130°C. The total weight

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loss of the films due to water desorption is listed in Table 2 and is estimated by determining the total weight loss from the polymer between the onset of heating and the temperature at which the rate of weight loss plateaus. This approximate method is reasonably sufficient for the purposes of this work. Using this method the highest water content of the polymer films occurred with H_2SO_4 (17%), MSA (12%) and $HClO_4$ (11%) dopants, whereas the polymer with the lowest water content was HCl, being 3%.

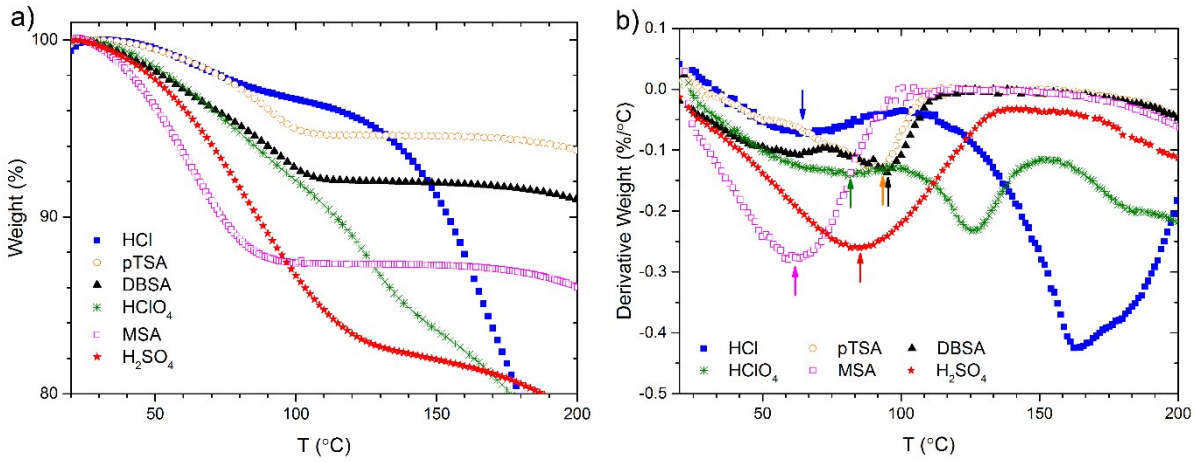

Figure 1. a) Thermogravimetric analyses between 20°C and 200°C for differently doped conducting polymer polyaniline films. Water desorption from all of the polymers begins at 30-40°C and is completed at different temperatures depending upon the dopant type. H_2SO_4 doped polymer exhibits the highest water content whilst HCl has the smallest water content. b) Derivative of the weight loss versus temperature. The arrows indicate the temperature of the maximum rate of weight loss from water desorption.

Dopant Type	**Moisture Loss (%)**
sulfuric acid (H_2SO_4)	17%
methane sulfonic acid (MSA)	12%
perchloric acid ($HClO_4$)	10%
dodecylbenzensulfonic acid (DBSA)	8%
para toluenesulfonic acid (pTSA)	5%
hydrochloric acid (HCl)	3%

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Table 2: Moisture content for polyaniline films with different dopants. The data is extracted from the thermogravimetric analyses in Figure 1 and is estimated by determining the weight loss from the polymer between the onset of heating and the temperature at which the rate of weight loss plateaus.

To investigate the role of the dopant molecule and moisture content on the current limiting properties surge protection devices were made based on the differently doped materials. Five to ten devices were made for each dopant type and the characteristic current-voltage effects observed were consistent across all the samples. Figure 2 shows current voltage sweeps of the devices from 0-10 V using a sweep rate of 4V/s with a step size of 1mV. A dotted line is included on the graph to show an ohmic response. A measure of the current limiting behaviour of the device can be made by comparing the current at 10 V with the current at the same voltage on the ohmic response. For example at 10 V the current of the H_2SO_4 doped polymer has been reduced by ≈53%. From the graph a strong correlation can be observed between moisture content of the films and the amount of deviation away from the ohmic response. The polymer devices showing the best to worst current limiting properties are the films having the dopants H_2SO_4, MSA, $HClO_4$, DBSA, pTSA and HCl. This is identical to the order for films with the highest to lowest moisture content (Table 2). The polymer with the highest moisture content H_2SO_4 has much greater current limiting properties than the MSA doped devices previously reported and exhibits negative differential resistance above 8 V. In contrast negative differential resistance was not observed in MSA doped devices even under high relative humidity conditions. HCl doped polyaniline interestingly exhibits the reverse effect, an increasing current with increasing voltage above 2 V. This effect was also observed in our previous report[14] but occurred when devices were measured under vacuum conditions, thereby having significantly reduced moisture content. Since HCl also exhibits very low moisture content we expect that de-doping from moisture loss during a current surge is not a significant enough effect to increase the resistivity of the film. Instead joule heating in the film acts to only increase the temperature which causes the current to increase because the materials conductivity

is strongly temperature dependent. This is a consequence of the conduction mechanism in conducting polymers which is a thermally activated process (variable range hopping).

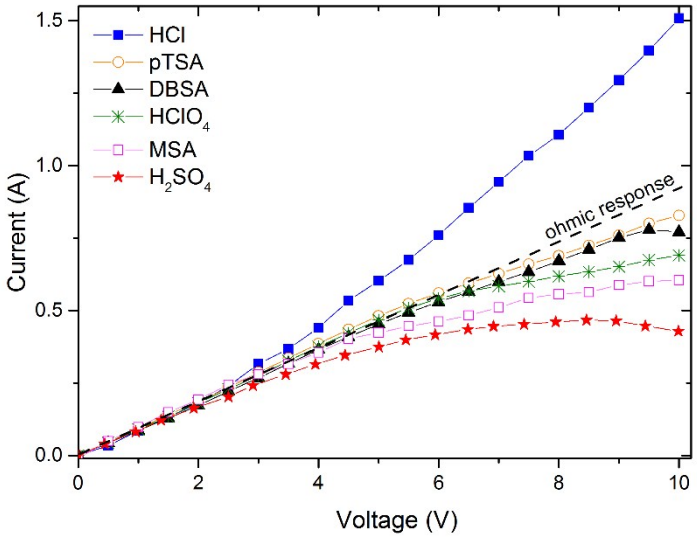

Figure 2. Current-voltage characteristics up to applied voltage of 10 V for differently doped conducting polymer current limiter devices in ambient air. For the H_2SO_4 doped polymer SAM the current limiting properties are greatly enhanced and exhibit negative differential resistance. The dashed line (ohmic response) acts as a guide to the eye.

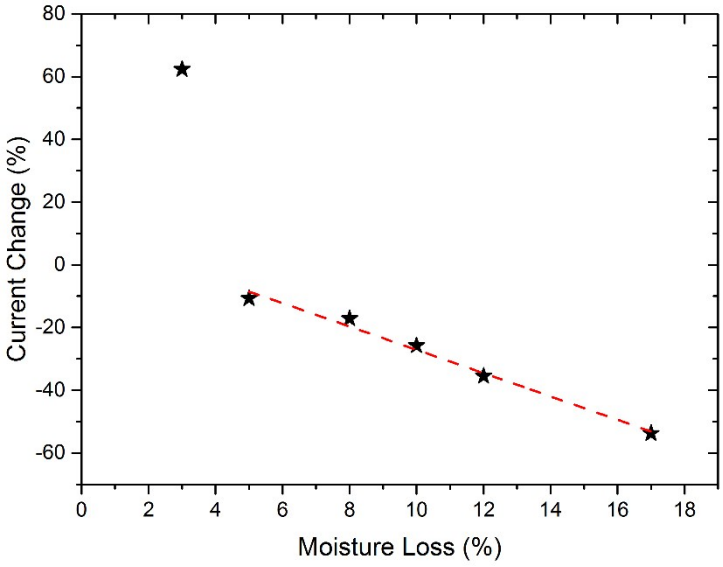

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Figure 3. Graph of the difference between the measured current and the ohmic current at 10 V (as a %) versus the moisture loss (as a %) for all six differently doped polymer devices. A linear relationship exists for devices that show current limiting properties whilst the HCl doped film, which instead exhibited an increased current at 10 V, does not fit the trend of the other polymers.

To demonstrate the relationship between moisture loss in the material and the current limiting properties of the devices Figure 3 shows a graph of the difference between the measured current and the ohmic current at 10 V (as a %) versus the moisture loss (as a %) for all six of the polymer films with different dopants. Five of the devices, those exhibiting current limiting behaviour, are plotted as having a negative change in current (a reduction) whilst the HCl doped is plotted as having a positive change (an increase) in current. For the devices showing current limiting behaviour a linear relationship exists between the current change and moisture loss in the films whilst the HCl doped polymer, which did not exhibit current limiting behaviour, does not fit the trend of the other polymers.

Previously we reported[21] that SAM modified gold electrodes changes the morphology of the polymer film directly adjacent to the electrodes leading to the formation of an interfacial compact thin film that lowers the contact resistance at the Au-polymer interface. This leads to enhanced current limiting properties due to a combination of lower contact resistance and increased joule heating within the interface region which during a current surge produces a current blocking resistive barrier due to a thermally induced de-doping effect caused by the rapid diffusion of moisture away from this region. The effect is exacerbated at higher applied voltages as the higher temperature leads to stronger depletion of charge carriers in this region resulting in a negative differential resistance effect. To investigate whether the current limiting properties of H_2SO_4 doped polyaniline devices could be further improved with this approach devices were made in which the gold electrodes were modified with a SAM of 1-dodecanethiol (DDT) $C_{12}H_{26}S$. Figure 4 shows the current – voltage characteristics of H_2SO_4 doped devices with modified and unmodified electrodes. The SAM modified device shows significantly

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improved current reduction in contrast to the unmodified device indicating that the same mechanism for current reduction similarly occurs in H_2SO_4 doped films.

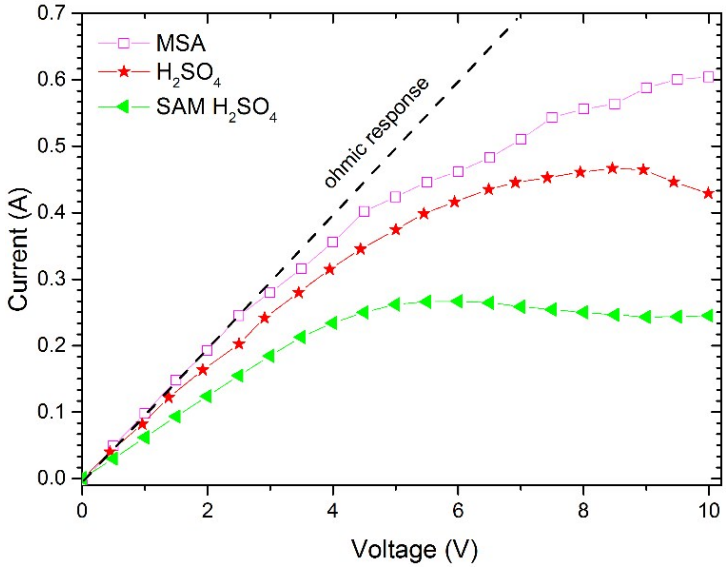

Figure 4. Current-voltage characteristics up to applied voltage of 10 V for MSA and H_2SO_4 doped polymer devices with unmodified electrodes and an H_2SO_4 doped polymer with electrodes modified with a self-assembled monolayer. The H_2SO_4 doped polymer exhibits significantly better current limiting properties than the previously reported MSA doped device but the addition of a self-assembled monolayer to the gold electrodes further improves the performance of the device.

To examine whether differences in polymer morphology could be the cause of the different current limiting properties in the doped films a study by scanning electron microscopy was used to investigate the morphology of the differently doped films. The results of the SEM study for all six dopants is shown in Figure 5. The SEM images indicate that the morphology of all of the polymers is open and porous with many voids interspaced between fibrous polymer material. Most of the doped polymers contain fibres with diameter typically in the region of 50-100 nm. This nanofibre spaghetti-like morphology has a high surface area to volume ratio that would be highly porous to gases, allowing gas molecules to quickly penetrate or exit the polymer, thus explaining the fast response of the devices and quick recovery.[14] DBSA doped polyaniline is more granular than the other polymers but the polymer network is still open with many voids which would allow moisture to diffuse rapidly out of the polymer. From

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this study no significant differences can be seen in the polymer morphology to account for the differences observed in the current-voltage properties. We note that in contrast some conducting polymers can have very different morphologies that are very dense and even semi-crystalline.[34,35,36]

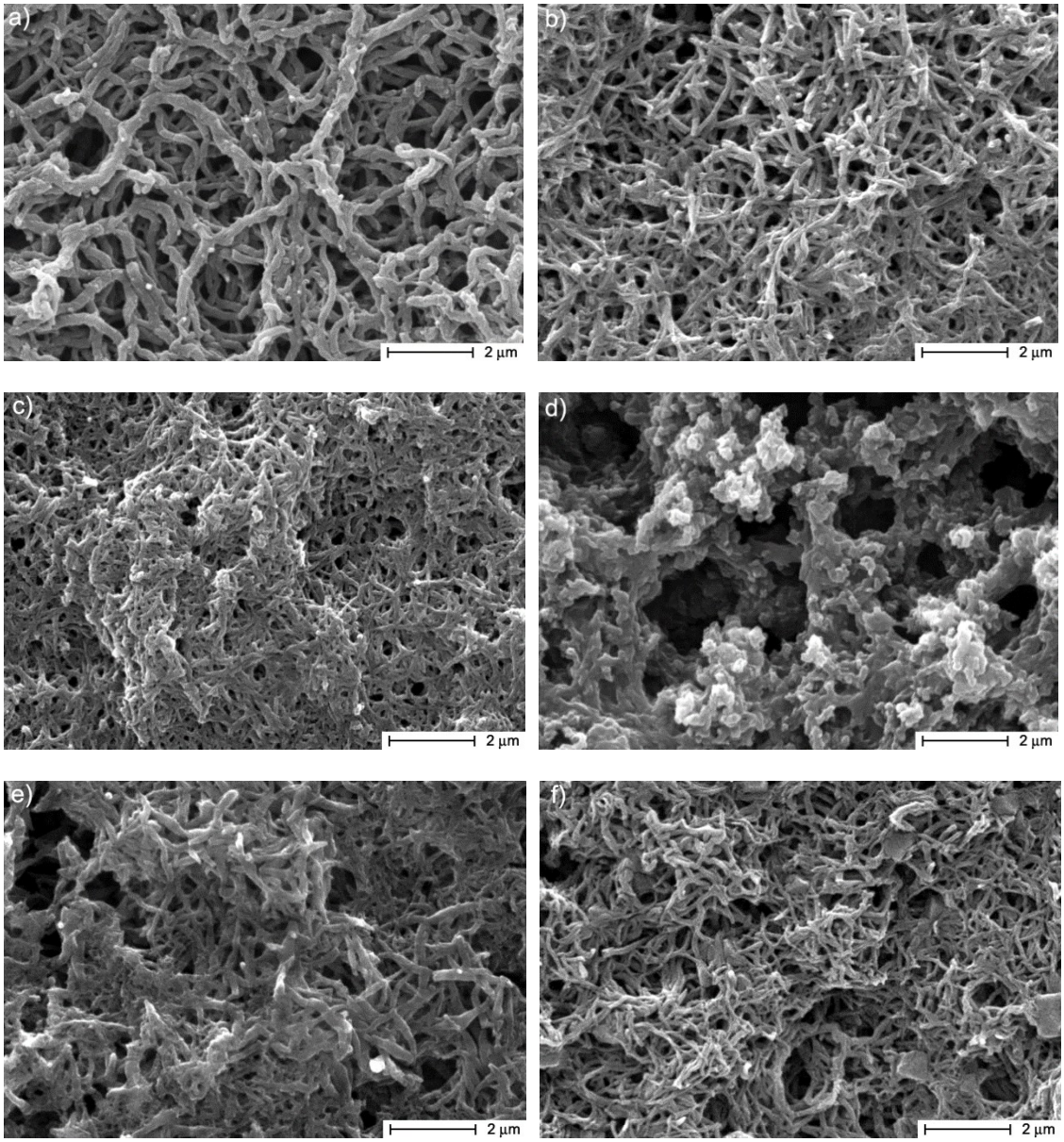

Fig 5. SEM images for the polyaniline films doped with a) methane sulfonic acid, b) sulfuric acid, c) hydrochloric acid, d)dodecylbenzenesulfonic acid, e) perchloric acid and f) p-toluenesulfonic acid.

Reliabilility of the H_2SO_4 doped conducting polymer devices was investigated by subjecting a freshly prepared device to continued current surges over a 36 h period. The current surges were spaced 10

minutes apart to give the device time to recover between surges. A fast 10V/s sweep from 0 to 10 volts was used to emulate a current surge. The graph in Figure 6 shows the current-voltage characteristcs of a typical H_2SO_4 doped ICP device over the 36 h period. Good current limiting behaviour with foldback properties from approximately 6 V onwards can be observed on all the current-voltage sweeps. The current-voltage sweeps during the first 12 hours indicate slighly increased levels of current at higher applied voltages. However from 12 hours onwards the device characteristics settle and behave consistently thereafter. The reason for this initial change is unclear but it is possibly due to irreversible changes caused by joule heating (e.g. removal of weakly bound dopant or remaining growth solution) or changes in some of the binding sites for water upon repeated desorption/adsorption. The latter effect has previously been observed in gas exposure studies on conducting polymers where it was shown that both reversible and irreversible effects occur in the polymer during exposure to gas and subsequent removal.[37,38]

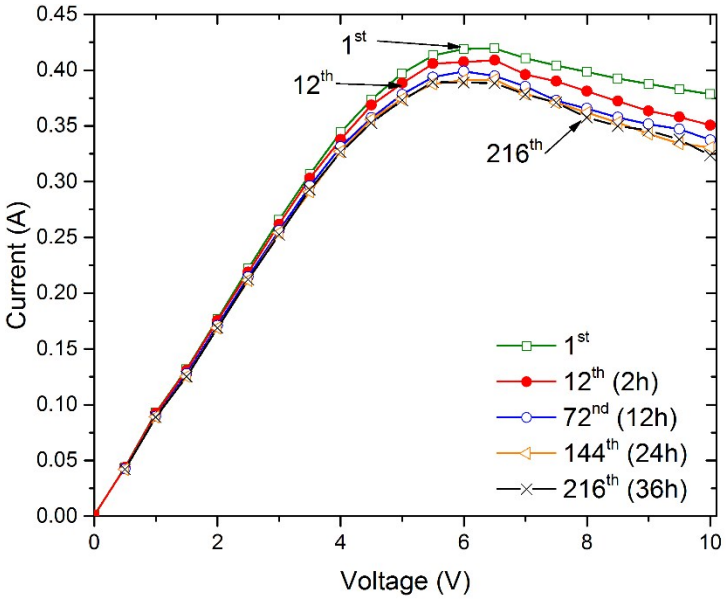

Fig 6. Current-voltage characteristics showing the long-term stability of a H_2SO_4 doped device over a 36 hour period. Fast I-V sweeps (10 V/s) were used to simulate the conditions of a current surge. The I-V sweeps occurred at intervals of 10 minutes for 36 hours.

4. Discussion

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Previous studies[39,40] have shown that a three step decomposition process occurs for protonated conducting polymers. The first stage of weight loss is due to water desorption. This is followed at higher temperatures by the protonic acid component and then at extreme temperature the polymer starts to degrade, producing gases such as acetylene and ammonia. In this paper we focus on TGA analysis from room temperature to 200°C. All of the polymers films measured exhibited different moisture content and temperature range over which water desorbed from the polymer. Of the six polymers DBSA, pTSA and MSA showed the most similar behaviour with water desorbing from room temperature completed by 110°C. Water desorption from H_2SO_4 doped polyaniline shows many differences. Water desorption similarly occurred from room temperature but the range over which the desorption occurred is much broader, peaking at 80°C and not completing until 130°C. Weight loss in the polymer continues from 130°C until a temperature that is greater than 200°C, albeit at a slower rate. However, this is most likely due to the desorption of protonating acid bound to the polymer chain, as has previously been reported.[33] H_2SO_4 doped polyaniline is also significantly different from the other polymers since it contains significantly more water than the other polymers, most likely this is explained by the strong hygroscopic nature of the H_2SO_4 molecule, having four strong polar ends. This can also explain its greater retention in the polymer at much higher temperature than the other polymers.

The desorption profiles of water from $HClO_4$ and HCl doped polymers is quite different from the other polymer films. For $HClO_4$ continuous weight loss occurs from room temperature to 200°C. An inflection to a larger rate of weight loss occurs at 120°C and this can be seen more clearly in the derivative of the weight loss (Fig. 1b). This possibly signifies a transition point from water loss in the film to the desorption of the dopant molecule, with the maximum rate of water loss most likely occurring at the very broad lower temperature peak at T=80°C in the derivate weight loss. Although water desorption in the polymer does not show a well-defined desorption peak the polymer overall undergoes a continuous and significant weight loss over this temperature regime, and by 180°C the total weight loss in the polymer is similarly to that of H_2SO_4. However, unlike H_2SO_4 there is no significant change

in the current-voltage properties which indicates that the weight loss between 100°C and 200°C is most likely desorption of unbound dopant or very weakly bound water. HCl doped polyaniline shows the smallest water content of the polymers measured. The derivative weight loss shows a broad peak at 65°C and at this temperature the weight loss of the polymer is only a few percent. By 180°C total weight loss from the polymer is as large as that occurring in the H_2SO_4 and $HClO_4$ doped polymers, however previous studies[33] have shown that weight loss above 130°C is the desorption of HCl. Some of the weight loss below 130°C may also not be all due to water desorption as studies have indicated that unbound HCl molecules also desorb at this temperature.[33]

The results from the thermogravimetric analyses (Fig.1) and current-voltage measurements on surge protection devices show a strong correlation between moisture content of the films (Table 2) and the current limiting properties of the devices. Devices with the smallest to largest current limiting behaviour had dopants in the following order H_2SO_4, MSA, $HClO_4$, DBSA, pTSA and HCl. This is identical to the order for polymer films having the highest to lowest moisture content. The film with the highest moisture content was H_2SO_4 doped and devices made with this doped polymer had significantly better current limiting properties. For the first time negative differential resistance was observed under ambient conditions and this effect was observed to be repeatable over a long period of time (Fig.6).

No major differences were observed in the morphology of the doped polymers so from this it is likely that the dopant molecule plays the dominant role in controlling water content in the films and also the temperature at which water desorbs from the polymer. The reason why differently doped polymers have different moisture content needs further investigation in order to determine the nature of the mechanism. Similarly, this should yield information as to why the temperature for water desorption is different in differently doped polymers. For example in MSA and DBSA doped polymers the moisture desorption is complete by 100°C and 110°C respectively, whereas in H_2SO_4 doped polyaniline water is still present up to 125°C. Qualitatively speaking this is most likely due to the different hygroscopic behaviours of the dopant molecule. However, this is complicated further as it is thought that water molecules are

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adsorbed at two different sites in polyaniline: the N-sites and the site of the dopant molecule. Interestingly the HCl doped polymer shows instead the opposite current–voltage relationship i.e. a large increase in the conductivity at higher applied voltage. This can be ascribed to the low moisture content in the polymer and resulting absence of the de-doping mechanism. Instead joule heating acts to only increase the temperature of the polymer which because of the nature of the thermally activated hopping conduction mechanism, leads to higher conductivity at high temperature. This effect is not as apparent in the other films since water desorption dominates the conduction properties of the polymer in this temperature region.

5. Conclusions

We report that thermogravimetric analyses and current-voltage studies on conducting polymer polyaniline films prepared with different dopants show a strong link between the dopant molecule and the current limiting properties of the films when used in surge protection devices. Six different polyaniline materials were investigated and large differences in their moisture content and temperature dependent water desorption profiles were observed. Moisture content varied between 3% and 18% and the temperature of the maximum rate of water desorption varied between 65°C and 100°C. Moisture content was shown to directly correlate with the current limiting properties of the films when used in surge protection devices under large current surge conditions. Films having low moisture content exhibited no current rectification while those with high moisture content demonstrated current saturation and foldback effects at high applied voltages. Polyaniline doped with sulfuric acid (H_2SO_4) exhibited the largest moisture content of the dopants tested and surge protection devices based on this have significantly enhanced current limiting properties with negative differential resistance occurring in ambient humidity conditions. This effect was further enhanced by using the method of interface engineering using self-assembled monolayers. In contrast polymer films with the lowest moisture content exhibited no current limiting behaviour and instead showed increasing current with increasing applied voltage. This effect had been observed in polymers with good current limiting properties but only after water had been removed by vacuum pumping. Thus we expect this reverse current-voltage

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relationship is due to Joule heating which in this case only acts to increase the temperature of the polymer which leads to higher conductivity because of the nature of the thermally activated hopping conduction mechanism. The identification of the dopant as the primary mechanism for controlling moisture content in the film and the switching properties of the devices should lead to further improvement of the devices and progress in the field.

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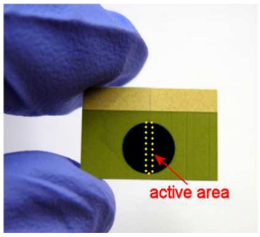

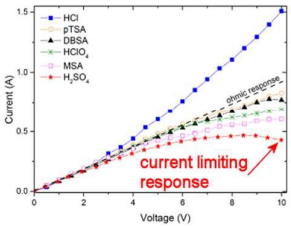

Significantly improved intrinsic conducting polymer surge protection devices through judicious choice of the dopant molecule.